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Baseline

Measurement of persistent organic pollutants (POPs) in plastic resin pellets from remote islands: Toward establishment of background concentrations for International Pellet Watch

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ABSTRACT

Plastic resin pellets collected from remote islands in the Pacific, Atlantic, and Indian Oceans and the Caribbean Sea were analyzed for polychlorinated biphenyls (PCBs), dichloro-diphenyltrichloroethane and its degradation products (DDTs), and hexachlorocyclohexanes (HCHs). Concentrations of PCBs (sum of 13 congeners) in the pellets were 0.1–9.9 ng/g-pellet. These were 1–3 orders of magnitude smaller than those observed in pellets from industrialized coastal shores. Concentrations of DDTs in the pellets were 0.8–4.1 ng/g-pellet. HCH concentrations were 0.6–1.7 ng/g-pellet, except for 19.3 ng/g-pellet on St. Helena, where current use of lindane is likely influence. This study provides background levels of POPs (PCBs < 10 ng/g-pellet, DDTs < 4 ng/g-pellet, HCHs < 2 ng/g-pellet) for International Pellet Watch. Sporadic large concentrations of POPs were found in some pellet samples from remote islands and should be considered in future assessments of pollutants on plastic debris.

Plastic resin pellets are granules, generally with the shape of a cylinder or a disk, <5 mm in diameter. As industrial feedstock for the production of plastic products, they are transported to manufacturing sites where they are re-melted and molded into a wide range of final products. Resin pellets can be unintentionally released into the environment during both manufacture and transport and can be carried by surface runoff and streams to the oceans. Plastic resin pellets have been found on many beaches around the world because of environmental persistence of plastic polymers, their capability for long-range transport, and increases in plastic production (e.g., Moore et al., 2001; Derraik, 2002; McDermid and McMullen, 2004; Ivar do Sul and Costa, 2007; Karapanagioti and Klontza, 2007; Ogata et al., 2009; Frias et al., 2010).

Plastic resin pellets sorb hydrophobic organic compounds, including persistent organic pollutants (POPs). Because of their ability to accumulate POPs with a concentration factor of up to $\sim 10^6$ relative to surrounding seawater (Mato et al., 2001), their ubiquitous occurrence on world beaches and their ease of collection and shipment, plastic resin pellets are used as passive samplers by International Pellet Watch (IPW; Takada, 2006). IPW is a volunteer-based global monitoring program designed to monitor the pollution status of the oceans and to understand the risks associated with chemicals in marine plastics. IPW has drawn global pollution maps of POPs and identified hot spots (Ogata et al., 2009; Karapanagioti et al., 2011).

To assess the analytical data obtained at individual locations it is important to understand the background levels of POPs (i.e., the levels of POPs in pellets from remote sites with minimal anthropogenic impacts). A comparison of POP levels from individual locations along with background levels would help to identify local

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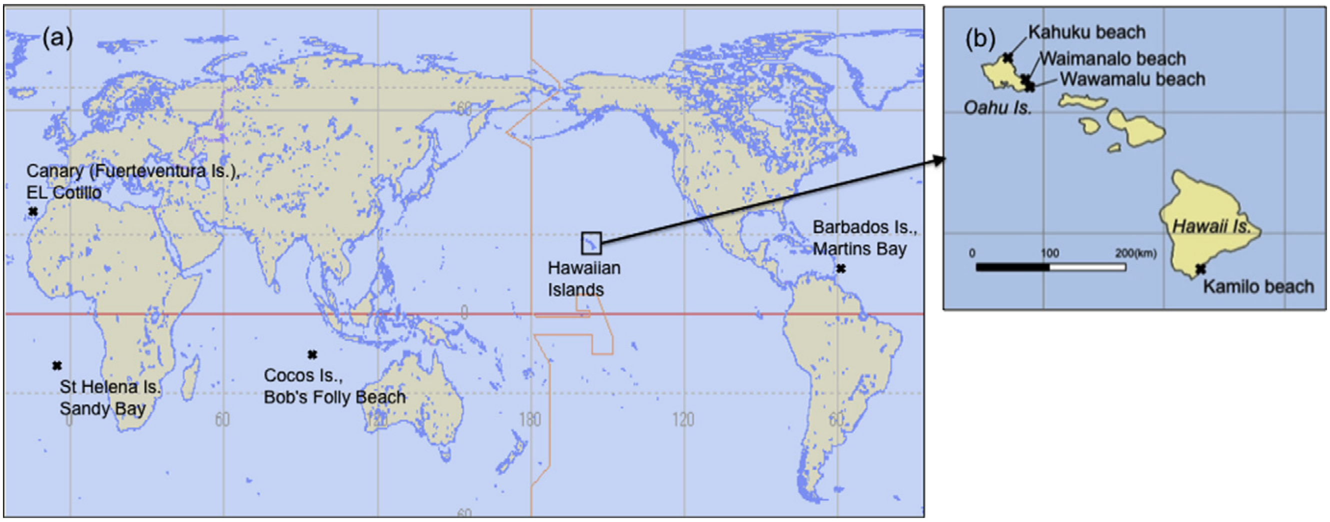

Fig. 1. Locations where plastic resin pellets were sampled.

Table 1
Sample information on collected plastic resin pellets.

Location		Latitude				Longitude				Date of sampling (YYMMDD)	Collector	Yellowing[a]
Island	Location name		Degree	Minute	Second		Degree	Minute	Second			
Canary (Fuerteventura)	EL Cotillo	N	28	40	11	W	14	0	40	100312	Angelika Heckhausen	Y
Oahu	Kahuku Beach	N	21	41	39	W	157	57	7	100506	Heidi Taylor	W
Oahu	Wawamalu beach	N	21	17	20.74	W	157	39	52.71	110522	Marvin Heskett	W
Oahu	Waimanalo beach	N	21	20	49	W	157	42	11	081019	Carey Morishige	Y
Hawaii	Kamilo beach	N	18	58	24.35	W	155	35	58	090729	Doug Young	Y
Barbados	Martins Bay	N	13	12	4	W	59	30	4	090512	Hugh Patterson	Y
Cocos (Keeling)	Bob's Folly Beach	S	12	8	45.63	E	96	49	31.28	090319	Taj Powell	Y
St. Helena	Sandy Bay	S	16	0	3.4	W	5	42	32.85	101010	Elizabeth Bailey	Y

[a] Y: yellowness of 40 or more; W: less than yellowness of 40.

or areal inputs of POPs. Here we analyzed pellet samples from beaches on remote islands to help establish these background levels.

Plastic resin pellets were collected from the Canary Islands (Spain), Saint Helena (British territory), Territory of the Cocos (Keeling) Islands (Australia), Island of Hawaii (US), Island of Oahu (US), and Barbados (Fig. 1 and Table 1). All islands are located in open ocean more than 100 km from the continents. Little or no industrial activity occurs near any of the sampling locations. Samples were collected from the high-tide line of sandy beaches and were picked up with soap-rinsed fingers or stainless-steel tweezers. Around 100 pellets were collected from each beach. The pellets were wrapped in aluminum foil, put into paper envelopes and sent to our laboratory in Tokyo via air mail.

Pellets were sorted and POPs were analyzed as described in Ogata et al. (2009), as follows. Immediately after arrival, pellets were sorted with a near-infrared spectrometer (Plascan-WTM OPT Research Inc., Tokyo, Japan) into polyethylene (PE), polypropylene (PP) and other polymers. Yellowing PE pellets were selected for chemical analysis; pellets with a yellowness of $\geqslant 40$ were selected, except among those from Kahuku and Wawamalu beaches, which were less yellowed. Median POP values were obtained by analyzing five pools of pellets (each pool consisted of five randomly-selected pellets) from each location.

POPs were extracted from pellets by soaking in hexane. The extracts were separated through fully activated silica gel columns into three fractions: Fraction I (*n*-alkanes and hopanes), Fraction II (PCBs and *p,p*′-DDE), and Fraction III (*p,p*′-DDT, *p,p*′-DDD, 4 HCH isomers [α, β, γ, δ], and polycyclic aromatic hydrocarbons [PAHs]). PCBs and DDE in Fraction II were determined by gas chromatography/ion-trap mass spectrometry. DDT, DDD, and the four HCH isomers in Fraction III were determined by gas chromatography/electron capture detector. The sum of all congeners quantified (i.e., CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206) is expressed as $\sum$13 PCBs. The reproducibility of this analytical procedure (i.e., column chromatography and instrumental determination) was confirmed by analysis of four aliquots from a single extract of pellets from Buenos Aires, Argentina. The relative standard deviations of the concentrations of the target compounds were 1–14%. Recovery was tested by spiking the aliquots of the extracts with authentic standards; recoveries were >95%. A procedural blank was run with every set analyzed (five pools). Analytical values <3$\times$ the corresponding blank were considered to be below the limit of quantification (LOQ). Smallest LOQs were 0.07 ng/g for $\sum$13 PCBs, 0.1 ng/g for DDT, 0.04 ng/g for DDE, 0.07 ng/g for DDD, and 0.4 ng/g for HCHs.

PCBs were detected in all pellet samples confirming their global dispersion through atmospheric and lateral transport from sources on land to open ocean. The within-sample variability at each location covered one to two orders of magnitude (Fig. 2). This variability is explained by the different residence times of individual pellets in seawater and the individual pathways of exposure to different concentrations of PCBs (Endo et al., 2005). To estimate representative concentrations at each location, we used the median concentrations of the five pools (Ogata et al., 2009).

In the previous study (Ogata et al., 2009), PCB concentrations in the pellets were well correlated with those in mussels collected from nearby locations to those of pellets, suggesting that IPW data

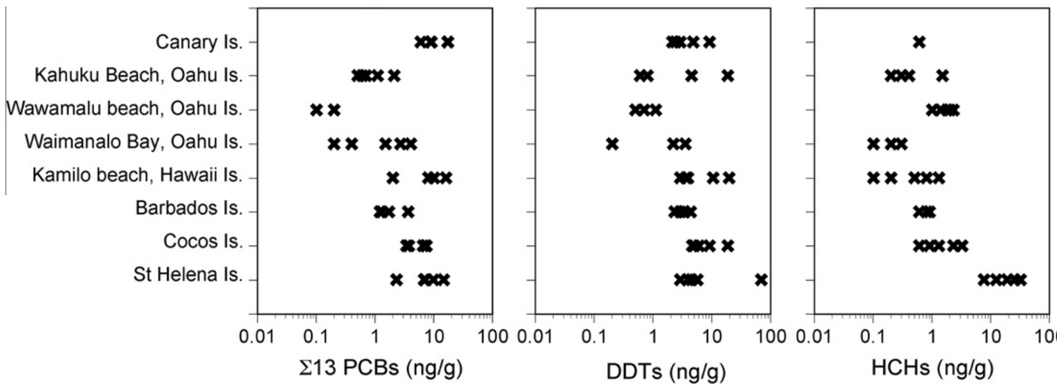

Fig. 2. Concentrations of PCBs, DDTs, and HCHs in individual pools of plastic resin pellets from the remote islands.

Table 2
Concentrations* of PCBs, DDTs, and HCHs in plastic resin pellets from the remote islands.

Location		PCBs**	DDTs				HCHs				
Island	Location name		DDT	DDD	DDE	DDTs***	α	β	γ	δ	HCHs****
Canary (Fuerteventura)	EL Cotillo	9.0	(0.7)#	0.9	2.5	4.1	0.0	0.6	n.d	n.d	0.6
Oahu	Kahuku Beach	0.7	n.d.##	0.1	0.6	0.8	(0.1)	n.d.	(0.3)	n.d	(0.4)
Oahu	Wawamalu beach	0.1	(0.6)	(0.1)	n.d.	(0.7)	(0.1)	(0.7)	(0.7)	(0.2)	(1.6)
Oahu	Waimanalo Bay	1.5	(0.5)	(0.3)	(0.1)	(0.9)	(0.1)	(0.1)	(0.1)	n.d	(0.2)
Hawaii	Kamilo beach	9.9	2.4	0.5	0.5	3.4	0.1	(0.1)	(0.2)	0.2	0.6
Barbados	Martins Bay	1.7	2.8	n.d.	0.3	3.1	0.2	n.d.	0.5	n.d.	(0.8)
Cocos	Bob's Folly Beach	6.5	2.8	1.5	0.8	3.4	0.1	0.6	(0.5)	0.5	1.7
St. Helena	Sandy Bay	7.0	2.8	0.6	0.5	3.4	0.7	(1.1)	15.8	1.6	19.3

* Median of five pools.
** Sum of concentrations of CB#66, 101, 110, 149, 118, 105, 153, 138, 128, 187, 180, 170, 206.
*** Sum of DDT, DDD, DDE.
**** Sum of α, β, γ, δ-HCHs.
# Value in parenthesis means below LOQ.
No peaks on chromatogram.

reflects pollution levels around measured locations. The median concentrations of $\sum$13 PCBs in pellet samples from the remote islands ranged from 0.1 to 9.9 ng/g-pellet (Table 2), 1–3 orders of magnitude smaller than those in pellets from industrialized coastal zones (hundreds of ng/g in Los Angeles, Boston, and Tokyo: Ogata et al., 2009). This is likely due to minimal industrial activities nearby which may release PCBs near the beaches of collection. Although PCBs were in use until they were banned in 1979 on the Island of Oahu, the beaches where pellets were collected are far from the industrial sites in the island. Kahuku, Wawamalu, and Waimanalo beaches lie on the east side of Oahu within 50 km of each other (Fig. 1b); however, PCB concentrations in the pellets from Kahuku and Wawamalu were one order of magnitude smaller than those from Waimanalo. The pellets from Kahuku and Wawamalu were less yellowed, meaning that they were relatively fresh and had not enough time to sorb PCBs to equilibrium. These variations in the characteristics of the pellets could be due to the large variations in ocean currents surrounding the Hawaiian Islands.

Median concentrations of DDTs (sum of *p,p′*-DDT, *p,p′*-DDD, and *p,p′*-DDE) ranged from 0.7 to 4.1 ng/g-pellet (Fig. 2 and Table 2). At four of the six locations where DDTs were detected, DDT was dominant over the degradation products (DDE and DDD), representing 70–91% of the total (Table 2). This dominance suggests current usage of DDT on the islands and/or spillage of stored DDT pesticide. Additionally, small but significant amounts of DDT could be used for mosquito control. DDTs concentrations found in the present study were one order of magnitude smaller than those in Indonesia, Thailand, and India and two orders of magnitude smaller than in Vietnam where the use of DDT to control malaria was suspected (Ogata et al., 2009). Thus, the use of DDT on the studied islands is likely to be minimal.

HCH concentrations were 0.2–1.7 ng/g-pellet except on St. Helena, where 19.3 ng/g-pellet was detected (Table 2). Similar low levels of HCHs were found in pellets from many other locations around the world (Ogata et al., 2009). The larger concentration on St. Helena is likely due to the current use of lindane (a scabicide) on the island. Among the four isomers, the γ isomer was predominant (>80%) in the pellets from St. Helena, supporting lindane as the primary source of HCHs.

Our results give tentative background levels of PCBs < 10 ng/g-pellet, DDTs < 4 ng/g-pellet, and HCHs < 2 ng/g-pellet in pellets. Because the studied islands are located in relatively remote oceanic areas and have little to no plastic manufacturing activities nearby, the majority of the pellets on the beaches likely come from sources outside of these islands. For example, the pellets collected on the shores of Oahu (Kahuku, Wawamalu, and Waimanalo beaches) were likely from exogenous sources (outside Oahu) and deposited by ocean currents and winds within the Pacific Ocean, primarily the North Pacific (Kubota, 1994). Interestingly, POP concentrations observed in the pellets on the remote islands were similar to those observed in plastic fragments collected in the open ocean by research vessels (Hirai et al., 2011). $\sum$13 PCBs in PE fragments from the Central Pacific Gyre ranged from 1 to 8.4 ng/g (Hirai et al., 2011). This range is similar to those in pellets from Hawaiian Islands (0.1–9.9 ng/g). $\sum$13 PCBs in PE fragments from the Caribbean Sea (8.4 ng/g) was similar magnitude to that in pellets from Barbados (1.7 ng/g). DDTs concentration in the PE fragments from the

Central Pacific Gyre (not detected to 2 ng/g; Hirai et al., 2011) and Caribbean Sea (4.8 ng/g) were similar to those in Hawaiian Islands (0.7–4.1 ng/g) and Barbados (3.1 ng/g), respectively. These consistencies may suggest that POP concentrations in the pellets from remote islands reflect POPs levels in the open ocean. Our previous study (Ogata et al., 2009), however, demonstrated that POP concentrations on stranded pellets reflect local pollution via the following mechanism: concentrations of POPs on pellets could be approaching concentrations that are in equilibrium with those found in seawater through sorption/desorption during their time spent drifting in seawater prior to stranding on beaches. Thus, POP concentrations in pellets collected from remote beaches reflect the pollution status around the sites of collection (i.e., remote environments with minimal anthropogenic activities). POP concentrations greater than the levels obtained by IPW would thus suggest local or areal inputs of POPs. Other than IPW, several researchers have also measured concentrations of POPs in environmental plastic resin pellets for monitoring and/or toxicological assessment (e.g., Frias et al., 2010; Colabuono et al., 2010; Van et al., in press). The background levels of POPs in marine plastics are useful for researchers. Because of the limited number of the samples, however, these background levels found in this study should be considered tentative. More samples from remote islands are needed to fully establish background levels. As these samples came from tropical and subtropical regions, to establish global background levels and especially to understand the effects of global distillation of POPs, pellet samples from remote islands at higher latitudes are required as well.

From an ecotoxicological point of view, the detection of sporadic large concentrations of POPs in some pellet samples (Fig. 2) is important. For example, we detected DDTs at 68.5 ng/g in one pool of pellets from St. Helena, but much smaller concentrations (2.9–5.6 ng/g) in the other four pools from there. The sorption/desorption of hydrophobic organic compounds to PE pellets is controlled by diffusion into the polymer matrix, and it can take as long as a year to reach equilibrium (Karapanagioti et al., 2010). The pellets with large DDT concentrations may have been exposed to DDTs in one area and been rapidly transported to the beach and stranded before the concentrations in the pellets had reached equilibrium with those in the seawater near the island. IPW's methodology of taking the median concentrations among five pools can exclude these sporadic large concentrations to give a reasonable estimate of the pollution status at a location. However, as organisms ingest all pellets, the arithmetic mean must be used in exposure analysis. In the case of DDTs on St. Helena, the arithmetic mean (17 ng/g) was five times the median (3.4 ng/g). Similar sporadic large concentrations of POPs were observed in plastic fragments collected from remote beaches (Hirai et al., 2011). Because concentrations of POPs in other environmental media (e.g., seawater, sediments, and biota) are at trace levels (e.g., sub pg/L, Gioia et al., 2008) in these remote environments, the sporadic large concentrations of POPs in the plastic debris may be more important as a pathway of exposure of POPs to biota in remote shores.

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